IN SEARCH FOR EXPERIMENTAL VERIFICATION OF (d+s) ORDER PARAMETER SYMMETRY IN OVERDOPED Bi2212

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0.1 Abstract

The field of research in high critical temperature superconductors has, next to a clear industrial application - for example in transportation of electrical current - the potential of being of considerable theoretical impact. The controversy it brings forth, within our understanding of how correlated electron systems behave, both on a macroscopic and microscopic scale, is large enough to produce a vast amount of theoretical output. This stems in the fact that it is expected that understanding superconductivity means understanding systems consisting of a large amount of electrons, which tend to behave in a mutual way. Why do researchers within condensed matter feel like this?

The interesting part lies in the fact, that the ground state of the cuprate superconductor - so near zero Kelvin, and without any induced mobile charge carriers - is a Mott insulator. Conventional band theory would describe the material as a conductor, however, it is observed to be an insulator. This is an argument to try to model a theory of high temperature superconductivity out of a correlated electron system viewpoint, due to the fact that band theory does not sufficiently incorporate the electron-electron interactions. Moreover, the copper based superconductors studied in this bachelor thesis order themselves with antiparallel oriented spins in their ground state, which is another strong argument for heading towards this direction.

The focus of this bachelor thesis is on trying to put one of the more daring theories within this field of interest to the test; a theory proposed by Zaanen et al. [1]. Since the discovery of high temperature superconductors, there has been extensive debate about the symmetry of the superconducting order parameter in these materials. For a certain class of materials called cuprates, a general consensus was reached, both experimentally and theoretically, that this symmetry should be $d_{x^2-y^2}$ (d-wave). Zaanen et al. proposed however, that upon strong hole doping of the cuprates, this symmetry gets further broken into $d \rightarrow d + s$ symmetry.

The fact that it has never been seen before, is largely due to two reasons. Namely, the theoretical calculations are simpler in the underdoped region, where the low concentration of charge carriers can be described as a dilute Bose gas. Secondly, from an experimental point of view, high concentrations of hole doping are difficult to achieve and the resolving power of the experimental equipment needs to be excellent, so that the induced s-wave component does not disappear in the uncertainties of the experiment. The approach of the research presented here, is to try to provide arguments against, or in support of the proposal by Zaanen et al..

For this research project, slightly lead overdoped $Pb_{x}Bi_{2-x}Sr_{2}CaCu_{2}O_{8+\delta}$ (Pb-Bi2212) samples have been measured through angle-resolved photoemission spectroscopy (ARPES). Furthermore, an overview is presented of the theoretical construct behind high temperature superconductivity, in order to provide some basic understanding of what is actually measured. Also, a chapter is included with general theory and typical setup used with UHV (order $\sim 10^{-11} mbar$) technologies such as ARPES and LEED. After connecting theory with the actual experiment, we conclude with presenting the measured data, discuss the results and draw conclusions.
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0.2 Introduction

In this report on the research that has been carried out, some light is shed on the nature of the pairing symmetry within cuprate high critical temperature superconductors. These cuprate superconductors are widely accepted to possess a certain symmetry, called \( d \)-wave symmetry, however, the theoretical condensed matter physical community still sees room for adjustment with respect to this numerously verified symmetry. This is largely due to the fact that a lot of the physics of high critical temperature superconductivity is still to be understood. Doing angle-resolved photoemission spectroscopy on these superconducting samples, is one of the most direct methods of unveiling the nature of the superconducting state, and bridges the gap between theorists thinking up ideas, and experimentalists, verifying or falsifying them in physical reality.

This report begins with a chapter intended to put the conceptual ideas behind superconductivity on a more stable basis. A section is included on the conventional theory of superconductivity, called BCS theory. Also, an elaboration on the superconducting order parameter is given, and what physical quantity it describes. After that, the leap is taken into high temperature superconductivity, and it is tried to build up some understanding on the theoretical background of this field.

Then there follows a chapter in which the theory behind the experimental tools is introduced, that have been used in the lab to probe the surface structure of the crystals studied and the pairing symmetry in the superconducting crystals.

In chapter 3 it is tried to connect the two previous chapters on theory of superconductivity and theory of the experimental tools, so as to produce a framework of understanding, in which the reader hopefully is able to have an understanding of what to measure, and how to measure. Also included is a section on the samples used, and what methods that have been employed in analysing whether the theoretical prediction by Zaanen et al. is borne out by the data.

In chapter 4 our data taken at the FAMoS and \( 1 \top \) ARPES measuring facilities is presented, results are discussed and conclusions are drawn.

Revision 15 October 2009: Added popular Dutch abstract.
Chapter 1

Theory on conventional and high temperature superconductivity

The purpose of this section is to give an understanding of the $d+s$ symmetry of the superconducting order parameter, within the context of this research. A broader understanding will be given of this symmetry, and when it is expected that the $s$-wave component will mix in with the "standard" $d$-wave symmetry, of the high $T_c$ superconducting (HTSC) order parameter within the cuprate superconductors.

The symmetry of the HTSC order parameter within the cuprates - also called gap symmetry, described in section 1.1.3 - is something that has been extensively studied since the discovery of HTSC.

The conventional theory of superconductivity by Bardeen, Cooper en Schrieffer from 1957 will be taken as a starting point. This theory, also known as BCS-theory, describes superconductivity on a microscopic level, first seen by Heike Kamerlingh Onnes in 1911, shortly after the liquification of helium. Some important concepts, which also apply in the theory of HTSC, are better understandable within this framework.

After describing BCS and Ginzburg-Landau theory in a rather qualitative way, the leap to HTSC will be made, involving the highly interesting physics behind antiferromagnetism, doping, Mott insulators, spin-charge separation, resonating valence bonds and lots of other exciting material.

It should be stressed that this bachelorthesis is not meant as a full theoretical study on the subject, and that the emphasis will be on the experimental results and analysis of these results. Therefore, only the theory needed to interpret the results in a proper but rather qualitative way, presented in the next chapters, will be described in this section. The author would like to encourage the reader to refer to the references at the end, for further reading about the subject and the exciting physics behind the subject of HTSC.
1.1 BCS theory of conventional low Tc superconductors

The observation of the sudden disappearance of all resistance within certain metals as of 1911, opened up a whole new field within condensed matter physics. Soon after the discovery of superconductivity, a lot of interesting phenomena were found. To name a few: the London equations describing the electromagnetic fields of a superconductor, or the Meissner-effect, which entails the total exclusion of an external magnetic field from within the superconductor [2].

However, no satisfactory microscopic theory describing the origin of the zero resistance in these superconducting materials were found, until in 1957 Bardeen, Cooper and Schrieffer came forward with their BCS-theory, 46 years after the first discovery of this phenomenon.

1.1.1 A physical basis for pairing of electrons

The whole idea behind BCS theory is that at sufficiently low temperatures, it is energetically advantageous for electrons in a solid near the Fermi surface, to form pairs with opposite and equal momenta. This attractive interaction between two particles which feel their repulsive Coulomb force, is due to the interaction between the electrons and the lattice vibrations (phonon scattering). As will be seen in a moment, these pairs consist of two electrons, one with spin up and one with spin down, to form a spin zero composite boson, and are called Cooper pairs.

Figure 1.1: Two electrons just outside a 2D Fermi surface with equal and opposite momenta. Adapted from [3]

As a starting point a Fermi sea of electrons is considered at \( T = 0K \), and two electrons are added to it, only interacting with each other through the Pauli exclusion principle and not with the sea [4]. As a second requirement both electrons are demanded to have opposite but equal momenta. This enables to write the wavefunction describing these pairs of electrons as

\[
\psi_0(r_1, r_2) = \sum_k g_k e^{i \mathbf{k} \cdot \mathbf{r}_1} e^{-i \mathbf{k} \cdot \mathbf{r}_2}
\] (1.1)

with \( g_k \) being certain weighting coefficients.

As a result of the requirement that the electrons have equal but opposite momenta, the center of mass does not move, see Fig. 1.1. And when identifying relative coordinates \( r = r_1 - r_2 \) and center of mass coordinates, one can write 1.1 as
\[ \psi_0(r) = \sum_k g_k e^{ik \cdot r} \] (1.2)

Because the antisymmetry of a wavefunction describing a system of fermions needs to be included when exchanging two constituents, equation 1.2 can be written as the product of an even spatial part \( \cos(k \cdot r) \), originating from the complex exponential in 1.2, with the odd singlet spin function \( (\uparrow \downarrow - \downarrow \uparrow) \):

\[ \psi_0(r) = \left[ \sum_{k > k_F} g_k \cos(k \cdot r) \right] (\uparrow \downarrow - \downarrow \uparrow) \] (1.3)

where only over de \( k \)-values is summed greater than the Fermi level, because that requirement was demanded earlier in this section.

By inserting this wavefunction in the Schrödinger equation for this problem,

\[ -\frac{\hbar^2}{m} \nabla^2 \psi_0(r) + V(r) \psi_0(r) = \epsilon \psi_0(r) \] (1.4)

with \( \epsilon = 2E_F + \epsilon \) - because one looks for two electrons near the Fermi surface with negative \( \epsilon \) - it can be shown that within the so-called weak-coupling approximation bound states do exist, with energy

\[ \epsilon \approx 2E_F - 2\hbar \omega_D e^{-2/N(0)V} \] (1.5)

Here \( N(0) \) is introduced to be the density of states at the Fermi surface, and \( V \) a constant potential within the range of a cutoff energy \( \hbar \omega_D \) away from \( E_F \), with \( \omega_D \) being the Debye frequency. With equation 1.5 it is easy to see that it will cost an energy \( 2\hbar \omega_D \) to destroy a Cooper pair. The energy of our pair against the ground state is \( \epsilon = 2E_F - \Delta \), where \( \Delta \) is the binding energy of the composite boson. So when using 1.5, the binding energy of the Cooper pair is easily identified to be

\[ \Delta = \frac{2\hbar \omega_D}{e^{2/N(0)V}} \] (1.6)

This binding energy is closely related to the superconducting energy gap, which shows itself as a shift of the leading edge of the electron occupancy, near the Fermi surface in a superconducting material. This energy gap is for conventional superconductors constant throughout the Fermi sphere, being of so called \( s \)-wave symmetry. However, for the cuprate superconductors used in this research, this is not the case, and other \( k \)-dependent gap functions can be seen. The physics behind the energy gap, will be discussed and linked to the superconducting order parameter and experimental environment more precisely in section 1.1.3 and 3.1.

1.1.2 Bound states originating from interactions with the ion lattice

In section 1.1.1 it was outlined that for a potential \( V \), electrons with antiparallel spin near the Fermi level, with opposite but equal momenta are able to form pairs (Cooper pairs or pairons) and thus condensate into a composite boson. Only until now nothing was mentioned about the nature as regarding to the origin of the attractive potential \( V \).

Considering the Coulomb force, it is evident that it is repulsive between two electrons, diverging for the relative distance of the electrons going to zero. The screening effect of the environment of

\( Of course the sinusoidal spatial part with an even spin function can be considered. Though hoping for an attractive interaction, the cosine will place the electrons closer together due to the larger probability amplitude around the origin.
our solid can also be taken into account which causes the divergence at the origin to take on a finite number, but this still does not account for any attractive interaction.

Within BCS theory, an attractive force is only felt when one looks at an electron in the conduction band, interacting with the positive ions on the lattice. Effectively polarizing the medium in its near vicinity by exercising an attractive force on the positively charged ion cores, this higher local charge density is felt by electrons nearby and a pair is formed, because a second electron can lower its energy by taking advantage of the lattice deformation. See Fig. 1.2.

Figure 1.2: An electron interacting with the positive ions on the lattice surrounding it, thus making its surroundings net more positively charged. Adapted from [2].

Summarizing; one has two electrons with opposite spin, which are bound together by electron-phonon interaction, see Fig. 1.3. The Cooper pair is now a composite boson, formed near the Fermi surface, which can condense into the ground state, because the wavefunction is now symmetric under particle interchange. This causes an energy gap to form of magnitude \( E_g \simeq 3.5k_bT_c \), due to the bosonization of the electrons into pairons near the Fermi surface.

Figure 1.3: Interaction with the lattice vibrational modes of two electrons, mediated through the exchange of a phonon. Adapted from [2].

\(^2\)Which is a famous mean-field result. \( E_g \simeq \frac{2\Delta}{k_bT_c} \).
1.1.3 Ginzburg-Landau theory and the superconducting order parameter

Before even Bardeen, Cooper and Schrieffer published their ideas in their famed theory on superconductivity in 1957, see [5], a lot was already known about superconductors. A vast basis had already been set as mentioned earlier by e.g. the work of the brothers London. Also, a more phenomenological theory than BCS theory was created by Ginzburg and Landau. Which was able to give nonetheless an accurate description of superconductivity. It incorporated lots of the effects seen in the laboratory, without giving a description of the microscopic machinery behind the infinite conductivity.

What Ginzburg and Landau did was - instead of describing a pairing mechanism and treating the electrons in single particle wavefunctions - assume the electrons to be in some kind of superconducting state, and work their way from that. To describe these superconducting electrons, they introduced a complex valued pseudowavefunction, known as the superconducting order parameter, \( \psi(r) \), with the property

\[
\psi(r)^* \psi(r) = n_s(r)
\]  

(1.7)

and \( n_s(r) \) being the local superconducting particle density. Many of the macroscopic phenomena observed, can be dealt with by considering the Cooper pair as a point particle with charge \( 2e \) and mass \( 2m_e \), only depending on the center of mass coordinate. This order parameter thus describes a field. At each point \( r \), \( \psi(r) \) tells us the way our system behaves as a whole, without bothering about all the electrons individually. Why is this useful? Well, most of the time, a system lowers its energy when its order parameter is uniform throughout space. Meaning that its symmetry is broken the same way throughout this space. However, materials don’t tend to break symmetry uniformly, like in the case of iron for instance. Iron is not magnetic by itself, however, one can align the constituents of this magnetic behavior - the spins within the material - in a parallel way, and suddenly the material becomes macroscopically magnetic.

After Gor’kov [6] showed in 1959 that the Ginzburg-Landau (GL) theory was in fact a limiting case within the BCS framework, new attention was paid to this theory, which resulted in the observation that the order parameter \( \psi(r) \) was found to be proportional to the gap parameter \( \Delta(r) \) [4]. However, in the context of superconductivity, the order parameter of the system is a little bit more subtle, than in the case of the magnetization example mentioned earlier. Loosely speaking, when considering the superconducting order parameter \( \psi(r) \), it represents a field describing a single state wave function for the condensate, occupied by a large number of the superconducting Cooper pairs.

It is important to note that \( \psi(r) \) shares the same angular symmetries as do atomic orbitals\(^3\), and can thus be expanded in spherical harmonics \( Y_{lm} \) [7]. One can thus speak for instance of s-wave (\( l = 0 \)) symmetry, or d-wave (\( l = 2 \)) symmetry. All known conventional superconductors possess spherical symmetry (\( l = 0 \)), but when entering the field of cuprate high \( T_c \) superconductivity, this symmetry is not \textit{per se} conserved, and the superconducting order parameter can take on also other symmetries for finite value for \( l \).

What’s most striking about this order parameter is that one only needs a function defined by just two coordinates, to describe the mutual physics behind \( \sim 10^{29}/m^3 \) electrons. When thinking about

\(^3\)One should not stretch this similarity too far.
BCS as a mean field theory, $\psi(r)$ would represent the mean field.4

Now that we are comfortable with most of the important concepts of superconductivity, let’s try to get a grasp of the difficulties high $T_c$ superconductivity brings along.

### 1.2 High Tc superconductors: the physics of doped Mott insulators

By the time that the majority within the physical community were comfortable with the way BCS theory explained the physics behind superconductivity, most of the physicists were confident that the roof of the successful BCS theory had been reached in 1973 with the $T_c$ of Nb$_3$Ge at 23.2K.

It was certainly not foreseen that superconductors with a critical temperature in the order of 100K would possibly exist. Hence, the discovery of cuprate high $T_c$ superconductors by Müller and Bednorz in 1986 came quite as a shock. What their superconductor, and all the later discovered cuprate superconducting materials have in common, is that they all possess copper oxide planes within their unit cell [8]. Hence the more common name for these superconductors: cuprates.

In the sections at hand, what is thought to be the machinery of the superconducting phase within these materials is described in more detail, and a model is communicated describing this machinery. In chapter 3 the theory we are going to treat here, and from the past sections, is connected with the experiment ultimately carried out in the Bachelor project.

#### 1.2.1 The breakdown of conventional band theory

The scientific importance of researching these cuprates, is not only because of the possible important industrial applications they can possess, but also because of the intellectual crisis they brought and bring forth in the quantum theory of solids. While conventional one-electron band theory has been very successful in describing ordinary metals and semi-conductors, undoped cuprates are all Mott insulators. This means that the solid is expected to behave as a metal, following conventional band theory, but in fact does not conduct electricity, possessing an energy gap of order $2eV$.

The reason for this is that these materials are highly correlated electron systems, and in band-theory the consequent strong electron-electron interactions are not adequately treated. The crystal structures of the cuprates have the common features of sheets of copper oxide between which there are divalent and trivalent ions. The superconductivity in the normal state is highly anisotropic, with much higher conductivity in the plane of the sheets than in the transverse direction [9].

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4It is important to make this observation, because the theoretical description of the HTSCs is done through mean field theories. More on this down in section 1.3.
Moreover, when looking at the cuprate phase diagram in Fig. 1.4, one can notice that the undoped state is antiferromagnetically ordered. This is an important indication that the behavior of the cuprates, is indeed to be understood by taking a closer look at the the strong electron-electron correlation within the materials and their mutual interactions. One sees also that when the cuprate is doped by inserting holes or electrons in the parent compound, at reasonably low temperatures, one enters a region of superconductivity, called the superconducting dome. The parent compound is therefore said to be close to an insulator-metal transition. Upon further doping, one leaves the superconducting dome, and the material will behave like a "normal" metal.

So what is needed, is a model describing near $T = 0$ and with $x = 0$ in the phase diagram an antiferromagnetically ordered ground state, where, as we bring in local charge carriers, a superconducting state is formed. Shortly said, the physics behind HTSC is the physics behind doping a Mott-insulator. This results in a theory were initially the antiferromagnetic order should be described in a satisfactory way. Besides some extremely strong coupled BCS-like theories, where the pairing is still described using phonon mediated pairing, it can be fruitful to work from theories that favor a pairing mechanism of magnetic origin. The resonating valence bond (RVB) theory proposed by Anderson in 1987 is such a theory.

1.3 Constructing a theoretical framework for HTSCs

What will be done in the chapter at hand, is take the so called Hubbard model, which describes the microscopic dynamical behavior of the valence electrons. The strong-coupling limit of the Hubbard model is better known as the $t - J$ model, which was further explored and extended by among other Wen and Lee [11]. The whole proposition by Zaanen et. al. of $d + s$ wave order parameter symmetry [1], rests on the extension to a $SU(2)$ gauge theory by Wen and Lee of the $t - J$ model. Also, the magnetic exchange energy in the cuprates, $J$, is about four times larger than the phonon energies $\hbar \omega_D$. So magnetic mediated pairing, with a $T_c$ proportional to $J$, would yield higher $T_c$ values [8] and is thus favored by some in solving the HTSC puzzle.

After looking at these models, we would like to direct our focus to the RVB state wavefunction, describing the antiferromagnetic ground state of doped Mott insulators.
1.3.1 Describing the spin-$\frac{1}{2}$ AF background through the Heisenberg model

One of the fundamental problems one encounters in understanding parts of condensed matter physics, is constructing a description of the ground state.

To tackle this question for our AF ordered Mott insulators, the interaction between the particles need to be modelled. In the cuprate case, one can imagine a simple model of the copper-oxygen plane as being a two dimensional lattice, with exactly one electron per site, which is a spin-$\frac{1}{2}$ particle. This is called half-filling. The system is still undoped and the spin carrying particles are allowed to interact with each other.

The spin degrees of freedom of this half filled electron system can be described by the spin-$\frac{1}{2}$ AF Heisenberg model. The corresponding hamiltonian reads:

$$H_{\text{Heis}} = -\sum_{\langle i,j \rangle}^{} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

where the summation is over all pairs of $i$ and $j$, and a symmetric coupling constant $J_{ij} = J_{ji}$ is introduced which is the exchange integral over the two spin-$\frac{1}{2}$'s on site $i$ and site $j$ being neighbors. So $J_{ij} = J$ for spins $i$ and $j$ being neighbors, and $J = 0$ else. Thus,

$$H_{\text{Heis}} = -J \sum_{\langle i,j \rangle}^{} \mathbf{S}_i \cdot \mathbf{S}_j$$

If $J > 0$, one can easily see that the state obtaining the lowest energy is the one in which all the spins are aligned parallel. Through the Pauli exclusion principle, the spins are not allowed to hop to a site were there is already a parallel aligned spin, so this ordering lowers the total energy of our spin lattice. For $J < 0$, antiferromagnetic ordering is found, because a spin on site $i$ lowers its energy by hopping to site $j$. Therefore, antiparallel spins are required. This is a strong argument for this type of insulators, why it is energetically advantageous for the system to order itself antiferromagnetically.

Here is a model describing the antiferromagnetic background, being exactly the undoped Mott-insulator encountered earlier, as the structure the parent compound finds itself in.

1.3.2 Transition to the Hubbard Hamiltonian

To extend the problem, charge carriers are now included in this spin-$\frac{1}{2}$ background by doping. One looks at the phase diagram in Fig. 1.4 for $x \neq 0$. For this it is needed to incorporate a new hamiltonian. This has to be a hamiltonian, for which if we look at large on site repulsion strengths, one
can get back the Heisenberg hamiltonian. This hamiltonian is called the widely studied Hubbard hamiltonian:

\[
H_{\text{Hubb}} = -t \sum_{<i,j>} \sum_\sigma (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} \tag{1.10}
\]

where the first term is the kinetic energy term with \( t \) the hopping parameter, \( c_{i\sigma}^\dagger \) and \( c_{j\sigma} \) the creation and annihilation operators for an electron on lattice site \( i \) and \( j \) with spin \( \sigma \), and \( n_{i\sigma} \) the number operator on site \( i \) with the general relation \( c_{i\sigma}^\dagger c_{i\sigma} = n_{i\sigma} \).

What the kinetic term does is to annihilate a one particle state on site \( j \) and create that state at site \( i \), summing over all the pairs and over all the spins \( \sigma \).

Furthermore, the second term in 1.10 is the potential energy term, taking into account the on site Coulomb repulsion when hopping to a nearest neighbor, \( U \). It was introduced by Hubbard as a simplification of the classical Coulomb potential. Just like with the Heisenberg model, a particle has to pay \( U \) to hop to a half filled site.

Now, for \( U \gg t \), the Hubbard hamiltonian can be turned into an effective hamiltonian called the Hubbard-Anderson hamiltonian. The Hubbard-Anderson hamiltonian reads:

\[
H_{\text{H-A}} = H_1 + H_2 + H_3 \tag{1.11}
\]

where

\[
H_1 = -t \sum_{<i,j> \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) \tag{1.12}
\]

is the old kinetic term and

\[
H_2 = \frac{2t^2}{U} \sum_{<i,j> \sigma} \left( c_{i\sigma}^\dagger c_{j\sigma} c_{j\sigma}^\dagger c_{i\sigma} - n_{i\sigma} n_{j\sigma} \right) \tag{1.13}
\]

\[
H_3 = -\frac{t^2}{U} \sum_{<i,j,k> \sigma} \left[ (c_{i\sigma}^\dagger c_{j\sigma} c_{k\sigma}^\dagger c_{j\sigma} c_{k\sigma} + c_{i\sigma}^\dagger n_{j\sigma} c_{k\sigma}^\dagger) + \text{H.c.} \right] \tag{1.14}
\]

The effect of these three hamiltonians on the charge carriers is without too much intellectual challenge, best understood through Fig. 1.6. One sees that the first hamiltonian \( H_1 \) just hops the charge carrier around from its own site to a neighboring unfilled site, or hole within the spin-\( \frac{1}{2} \) background. For the second two hamiltonians \( H_2 \) and \( H_3 \), the intermediate state encountered earlier in the Heisenberg model is gained again, at the cost of the same energy \( U \) in the Hubbard hamiltonian 1.10.

\[\text{Figure 1.6: Pictorial way of visualizing the effect of the three Hamiltonians } H_1: \text{ (a), } H_2: \text{ (b) and } H_3: \text{ (c) on the spin carrying entities situated on lattice sites. Adapted from [8].}\]
The number of nonzero matrix elements in $H_3$ is small, so if only the ground state is important, one might neglect $H_3$ [8]. In that case, the effective Hamiltonian can be written $H_{eff_{H-A}} = H_1 + H_2$. Secondly, one is able, not without some head-scratching, to transform $H_2$ in the already presented spin-$\frac{1}{2}$ AF Heisenberg Hamiltonian.

$$H_2 \Rightarrow H_{Heis} = J \sum_{<i,j>} (\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4})$$

(1.15)

with $J$ being $4t^2/U$ and the factor $\frac{1}{4}$ is introduced because of the transformation used to write $H_2$ in the Heisenberg hamiltonian form.

This new effective Hamiltonian $H_{eff_{H-A}} = H_1 + H_{Heis}$ is called the $t-J$ Hamiltonian, due to the potential term $J$ from the Heisenberg Hamiltonian, and the kinetic term $t$ in $H_1$. This $H_{t-J}$ is taken as the starting point in the paper by Wen and Lee [11].

$$H_{t-J} = H_1 + H_J = -t \sum_{<i,j>} \sum_{\sigma} (c_i^\dagger \sigma c_j^\sigma + H.c.) + J \sum_{<i,j>} (\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4})$$

(1.16)

### 1.3.3 The $t$-$J$ model and the RVB state

In the previous sections 1.3.1 and 1.3.2, it was encountered that the undoped half-filled system, described by the Hubbard model, was equivalent to a spin-$\frac{1}{2}$ AF Heisenberg model (1.9). Then how the introduction of charge carriers affected this Hubbard model was looked upon, and the transition was made to an effective hamiltonian, called the Hubbard-Anderson hamiltonian (1.11). After omitting $H_3$ (1.14), and rewriting $H_2$ as the Heisenberg hamiltonian, this was called the $t-J$ hamiltonian (1.16).

Now, one might ask what the physical link is, between this $t-J$ Hamiltonian and the geometry of the cuprate. The essential insight is, that the hole induced by doping, resonates on the four oxygen sites surrounding a copper atom, and the spin of the doped hole combines with the spin on the Cu site to form a spin singlet [11]. By focussing on the low-lying singlet, one effectively gets a one-band tight binding model on a square lattice, which is described in the large $U$ limit by the $t-J$ hamiltonian.

Studies on this hamiltonian confirmed that it describes a strong enough electron-electron interaction to produce a Mott insulating ground state at half filling. Besides that, the $t-J$ hamiltonian is thought by a significant sub-set of high $T_c$ physicists to captures the essence of the low-energy electron excitation within the cuprates.

It has been proposed by Anderson that the ground state of this hamiltonian is the so called resonating valence bond (RVB) state. This is a different state of matter than the Néel state, in which the ground state is formed by spins which align purely antiparallel. This is due to the crystal structure, which can force some spins to still align parallel, which destroys the pure Néel state, this is especially the case in the 2D lattice utilized here, which causes alignment problems when considering eg. a triangular lattice.
The RVB state consists of the net spin of two sites, coupled together in a singlet state, which pairs with another site into singlet pairs, which make up a so called valence bond. As a consequence of this bond, one observes two kind of quasi-apticle excitations. Spinons, which do not possess a charge, and are thus neutral spin=$\frac{1}{2}$ excitations, and holons, which are bosons without spin and a charge $\pm e$. This can be seen in the following way. For instance, if one takes a purely antiferromagnetic ordered background, and induces a charge carrier, like a doping induced hole. Now, this hole is mobile, and can hop between nearest neighbor lattice sites. However, when hopping through the lattice, it exchanges itself constantly with a spin carrier, and thus leave a frustrated lattice behind, in which the AF ordering is destroyed. This is called spin-charge separation. This means, that if the RVB state is the ground state of the highly doped superconductors, one can have different dispersion relations for our spin and charge quasi particles. By considering this, it is plausible to assume that the spinless holons, which are the charge carriers and bosons, can BCS condensate into the superconducting ground state.

The order parameter, describing the collective physics of these "condensates", presents itself in certain symmetries, depending on which theory one chooses to adopt. After all, only experiment can give us conclusive evidence in which direction we should look in successfully describing high temperature superconductivity.

This is the point were Wen and Lee take off in their review [11] about casting the physics behind the doping of a Mott insulator in a $SU(2)$ slave boson gauge theory, in which the holons are in the bosonic state with fermionic spinons. Within the $t-J$ model, this constraint is introduced to prevent for double occupation of half filled sites, which leads to the description of the theory within a gauge invariant framework called $SU(2)$. It is felt that the $t-J$ model and its RVB ground state describes the essence of the AF background and the effects caused by the introduction of charge carriers. The gauge invariance within this theory permits both $s$-wave and $d$-wave pairing symmetries for the cuprate superconductors. However, the idea of Zaanen and his group in Leiden, nested within the framework of the $SU(2)$ slave boson theory by Wen and Lee, is that the symmetry of the cuprate superconducting order parameter should be represented by a $d+s$ symmetry, were the $s$-wave is induced on entering the regime of higher doping. See Fig. 1.7 and 1.9.

Figure 1.7: Plot of the $SU(2)$ slave boson theory on high temperature superconductors allowed pairing symmetries. Adapted from [12].
As mentioned earlier, the physics of the underdoped cuprate superconductor may be very well described by a dilute Bose gas. However, upon further doping of the cuprate, the nature of the bosonic charge sector is not to be described in this regime anymore. This further insertion of charge carriers may be quite easily described in the \( SU(2) \) theory by Wen and Lee. The reason behind the induced \( s \)-wave component in this framework, is, as stated by Zaanen: "for deep and elegant reasons", so it is felt that it would be better not to get into this matter to much, and to direct the focus of this thesis to the actual experiment.
Figure 1.9: Theoretical predictions on the doping induced s-wave component within the cuprates. Adapted from [1].
Chapter 2

Theory on LEED and ARPES

In the next chapter at hand, the theory behind the two experimental setups used in this Bachelor project is introduced, that enables to extract lots of interesting data from the cuprate superconducting samples.

The first one to describe in section 2.1, Low-Energy Electron Diffraction (LEED), is a procedure in which the sample surface gets bombarded with electrons, resulting in a diffraction pattern resembling the lattice symmetries relevant for the surface of the samples. In the context of our study, LEED will be used merely as a qualitative method, used in this Bachelor research to orientate the sample used, and to orient in reciprocal space. This will be discussed further down in section 3.

The second setup described in section 2.2 is the heart of the research carried out in this Bachelor thesis. At this moment, Angle-Resolved Photoemission Spectroscopy (ARPES), is one of the most comprehensive tools in condensed matter research, providing detailed information about the electronic band structure at the surface of the sample studied with it. It gives insight into a lot of theoretical predictions in the HTSC field, due to the fact that it is an experimental technique that enables us to observe directly the energy and momentum distribution of electrons at the surface.
2.1 Low-Energy Electron Diffraction

Finding out the pattern in which atoms tend to order themselves within a certain material is one of the key steps in finding out and understanding the behavior of a material. One is interested in the atomic and electronic structure within a sample to explain phenomena, and LEED provides us with a tool to probe the surface area of those materials, both qualitatively and quantitatively.

Because the LEED device was used by us in a more qualitative fashion, a qualitative, inexhaustive account of some of the key concepts will be given here, sparing the reader an extensive elaboration on kinematic theory.

2.1.1 General theory behind LEED

As stated earlier, a LEED analysis is carried out by bombarding the surface of a sample, with a monochromatic beam of collimated electrons. This means that the bundle of electrons is nearly parallel, so when propagating over a certain distance in space, the bundle stays coherent.

This bundle of electrons can be described by a plane-wave, with a wavelength, which conforms to the following equation by de Broglie, describing the wavelength of matter waves:

\[ \lambda = \frac{h}{m_e v} = \frac{h}{\sqrt{2m_e E_{\text{kin}}}} \tag{2.1} \]

The kinetic energy of these electrons \( E_{\text{kin}} \), is in the order of tens of electronvolts up to several hundreds. This makes the wavelength of the electrons of the same magnitude as the lattice constants in solids. Due to this fact, Bragg diffractions are expected to show up, analogous with the X-ray case, for which Bragg found his famous formula:

\[ \sin \theta = \frac{n \lambda}{2d} \tag{2.2} \]

with \( \theta \) the angle between the propagation vector of the incoming plane wave and the surface normal, \( d \) the interplanar distance within the crystal, \( \lambda \) the de Broglie wavelength from equation 2.1 and \( n \) an integer number encoding the diffraction order.

What is learned is that LEED is surface dependent, and that the sine of the scattering angle \( \theta \) is inversely proportional to the square root of the kinetic energy of the electrons. One might think at this point that the electrons are somehow interfering with each other, showing up as a diffraction pattern. However, this is incorrect. Electrons cannot destructively interfere with each other resulting in their annihilation. The LEED pattern we encounter is the superposition of intensities, corresponding to individually scattered electrons.

Now, we can collect these spots of intensities on a phosphorus screen, where they will light up as bright spots in some ordered pattern. One might ask: What do these spots tell us about the way the atomic structure of our crystal in question orders itself? Like in X-ray diffraction, these constructive interferences are described by the Laue conditions.

\[ \mathbf{a} \cdot \mathbf{K} = 2\pi h \tag{2.3} \]

\[ \mathbf{b} \cdot \mathbf{K} = 2\pi k \tag{2.4} \]
\[ \mathbf{c} \cdot \mathbf{K} = 2\pi l \]  \hspace{1cm} (2.5)

with \(\mathbf{a}, \mathbf{b}\) and \(\mathbf{c}\) being the primitive unit cell vectors, \(\mathbf{K} = \mathbf{k}_f - \mathbf{k}_i\) the difference between initial and final wave vectors, and \(h, k, l\) the reciprocal lattice indices.

What can be seen is that the scalar products in equations 2.3, 2.4 and 2.5 describe a set of parallel planes, perpendicular to \(\mathbf{a}, \mathbf{b}\) and \(\mathbf{c}\). These planes intersect with each other, forming rods which can be projected onto a surface, forming a periodic set of points. By this method one is able to geometrically construct the reciprocal lattice of the real space crystal lattice, and the reciprocal lattice unit vectors, \(\mathbf{a}^*, \mathbf{b}^*\) and \(\mathbf{c}^*\), are defined in the following way:

\[ \mathbf{a}^* = \frac{2\pi \mathbf{b} \times \mathbf{c}}{\mathbf{a} (\mathbf{b} \times \mathbf{c})} \]  \hspace{1cm} (2.6)

\[ \mathbf{b}^* = \frac{2\pi \mathbf{c} \times \mathbf{a}}{\mathbf{a} (\mathbf{b} \times \mathbf{c})} \]  \hspace{1cm} (2.7)

\[ \mathbf{c}^* = \frac{2\pi \mathbf{a} \times \mathbf{b}}{\mathbf{a} (\mathbf{b} \times \mathbf{c})} \]  \hspace{1cm} (2.8)

Because of the rather low kinetic energy, LEED is very surface sensitive, and second order scattering events from within the material are more or less negligible. Due to this fact that LEED is surface sensitive, only equations 2.3 and 2.4 apply in first instance [13]. As a consequence of this, one has a reciprocal lattice plane, with rods extending perpendicular from each lattice point. Now, the requirement that can be put on the fact that constructive interference occurs, is that in a diffraction experiment, the values of momentum transfer where constructive interference occurs also form a lattice, namely, the reciprocal lattice.

![Figure 2.1: A schematic overview on how the Ewald sphere determines the direction of the observed scattered beams. Adapted from [13].](image-url)
Introducing energy conservation, it is clear that the lengths of $k_i$ and $k_f$ are the same, if one only considers purely elastic scattering. This means that the scattering vector describes a sphere of radius $\frac{2\pi}{\lambda}$, which is called the Ewald sphere, after the German physicist Paul Peter Ewald. If one now draws this sphere around the initial wave vector $k_i$, the intersection of this sphere with the reciprocal lattice rods mentioned earlier gives a pattern of points in 2D. From the center point of the Ewald sphere, every vector drawn to an intersection, is an allowed scattering vector. So, the intersections of the Ewald sphere with the reciprocal lattice defines our set of possible $k_f$, and thus the spots seen in a LEED measurement.

In short, the LEED pattern is a direct means of visualizing the configuration of the reciprocal lattice. The pattern increases\(^1\) with $\sqrt{E_{\text{kin}}}$, and through the Ewald sphere, the possible scattered beam directions can be linked to the experimental situation. By orienting the pattern one sees on a LEED experiment in a certain way, one is able by this means to orient in $k$-space. This makes LEED a valuable addition to ARPES measurements, because for any meaningful measurements carried out with ARPES, orientation in $k$-space is crucial.

### 2.1.2 Typical LEED setup

The typical LEED setup, is in contrast to modern ARPES facilities (see further down in section 2.2) quite straightforward. Moreover, it is strikingly similar to the experimental setups, used in the 1920's, in the first electron diffraction experiments. The underlying concept of how to setup and execute a LEED analysis, did not change much over the years. This is illustrated by a quotation of R.L. Park et al., cited from [13]: “It will be noticed that, in schematic form, the system bears a startling resemblance to that employed by Davisson and Germer in 1927. The changes that have taken place can be linked to those of the automobile over the same span of years. A number of convenience features have been added which are roughly equivalent to the electric wind shield wiper and automatic transmission.”

What one needs for a typical experimental LEED setup, is an electron gun, producing a monochromatic beam of electrons, which is aimed at the surface of the sample under experiment. The electrons will scatter at the surface, back to a luminescent screen to visualize their spatial distribution.

Because we do not want the electrons to scatter at air molecules, thus interfering with the collimated bundle, this experiment is carried out in a vacuum in the order of $\sim 10^{-7}$ mbar or higher. Also, because LEED is a very surface sensitive technique, this UHV makes sure the surface of the sample stays uncontaminated as long as possible.

Moreover, one needs some electron optics, for focussing the beam on the sample, and an electron energy selector that allows us to select for elastic scattered electrons only, consisting of a pass and a high pass filter, together forming a narrow energy window. Behind the electron gun, one sets up a screen of luminescent material, and this enables one to observe the lattice structure of the sample under experiment.

### 2.2 Angle-Resolved Photoemission Spectroscopy

By using ARPES, one is able to probe the electronic band structure of a certain material by direct means. It is based on the well known photoelectric effect, originally found by Rudolf Hertz in 1887. It \(^1\)Remember, this is reciprocal space, so not inversely proportional.
was observed, that by shedding light of a certain wavelength on two electrodes, sparks were created more easily. This effect was finally successfully explained by Albert Einstein in 1905, for which he was awarded the Nobel Prize.

In the next two sections, a description of ARPES will be given, and the reader is given some insight in how the electronic band structure is probed through using this measurement. In chapter 3 it is then finally described how to extract useful data through ARPES.

2.2.1 General theory behind ARPES

The first important task is to find the relation between the energy of the incoming photons shed on the surface, and the energy and momentum of the electrons that free themselves from the surface (called photoelectrons). A very rough first assumption, to give an upper limit for the energy, is of course by saying $E_{\text{kin}} = h\nu - \phi$. Here $E_{\text{kin}}$ is the kinetic energy of the photoelectron, $h$ is Planck’s constant, $\nu$ is the angular frequency of the incoming photon and $\phi$ the material work function\(^2\), which is the amount of energy that must be paid to free an electron from the material. This is due to the potential barrier that exist at the surface of the material being measured, that prevents the valence electrons from escaping. It is usually somewhere between 4-5 eV for metals [10].

In short what is done in ARPES measurements, is that the sample is placed on a sample holder, which can be adjusted over several axes. A beam of monochromatic light impinges on the sample, and the thus obtained photoelectrons are run through an electron energy analyzer. By this means, it is possible to measure the energy of the photoelectrons for different emission angles. Moreover, one knows that the classical relation between the modulus of the electron’s momentum and its kinetic energy, is given by $p_e = \sqrt{2m_e E_{\text{kin}}}$. So for the photoelectrons, the following set of two equations is derived:

$$E_{\text{kin}} = h\nu - \phi - |E_B| \quad (2.9)$$

$$p_\| = \frac{\hbar k_\|}{\sqrt{2m_e E_{\text{kin}} \sin \theta}} \quad (2.10)$$

where $E_B$ is introduced to be the binding energy of the electron, $m_e$ the electrons mass, $\hbar$ the reduced Planck’s constant, $k_\|$ the wave vector of the electron parallel to the surface, and $\theta$ the angle the analyzer makes with the surface of the sample, see Fig. 2.2.

What needs to be considered is that with this method one only can measure the $k$-component of the electrons parallel to the surface, so that is in the $x - y$ plane. This is due to the lack of translational symmetry along the surface normal [14]. This implies that, even by knowing all parallel momenta, one is never able to completely determine the wave vector $k$ without making additional assumptions. This makes the $E(k_z)$-dispersion relation of a material an important factor in determining whether it is very suitable for ARPES investigation or not. Suitable systems have large anisotropy in the crystal structure, with periodicity in the $z$-direction consisting of much larger interatomic spacing than in the $x - y$ plane. The cuprate Bi2212 superconductor studied in this research has in comparison to the dispersion in the $k_x$ and $k_y$ direction a negligible variation in $k_z$. The Fermi

\(^2\)Sometimes denoted $W$. 

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surface of the crystal has a cylinder like geometry, making the photoelectron’s momentum almost entirely determined by $k_\parallel$. So:

$$k_\parallel = \sqrt{\frac{2m_e E_{\text{kin}}}{\hbar^2} \sin \theta}$$  \hspace{1cm} (2.11)

What also needs to be considered, is the surface sensitivity of an ARPES measurement. Because electrons within the material have a mean free path before scattering at one or more nuclei, thus altering the photoelectrons initial kinetic energy and momentum, ARPES measurements are also very surface sensitive. By discriminating for photoelectrons again selected through a narrow energy window, one knows that the electron escaped close to the surface, making its measured values for kinetic energy and momentum more reliable. This makes the environment in which the measurements take place, again an important factor in the experimental setup, because the measurement is very sensitive to possible contamination at the surface. To limit this interference to a minimum, ARPES measurements are to be carried out in ultra high vacuum, which is in the order of $\sim 10^{-11}$ mbar.

![Figure 2.2: Geometry of an ARPES experiment as described in this section. Monochromatic light is shed on the sample, which is positioned under some angle with the electron analyzer. Adapted from [10].](image)

Now, putting all the bricks together, what is seen is that the angle at which the photoelectron leaves the material, is related to its momentum, as is its kinetic energy. And also, that by knowing the photoelectrons kinetic energy $E_{\text{kin}} = \frac{1}{2}m_e v^2$, one can look for $E(k)$ relations. In other words, by directly counting the number of electrons leaving the surface at a certain angle, as function of their energy (velocity), one has a very strong tool in mapping the dispersion relation at the surface of the material in question. By plotting these data in an $E$ versus $k$ graph, one is able to actually "see" the electronic band structure.

### 2.2.2 Typical ARPES setup

The monochromatic light used in the photoemission process, can be obtained by either using a gas-discharge lamp, or through synchrotron radiation. However, the use of synchrotron radiation is recommended over the use of a gas-discharge lamp. This is because one is able, with the use of synchrotron radiation, to achieve a continuous spectrum which can be turned into monochromatic light.
by monochromator. Unlike with the use of a gas-discharge lamp, which has a discrete spectrum, due to the fact that it uses electron excitation and absorption. This makes tuning to the photon energy $h \nu$ best suitable for the research less precise, see equation 2.9.

For the research carried out in this Bachelor thesis, both a gas-discharge was used, and synchrotron radiation powered ARPES facilities. The FAMoS microscope situated in the van der Waals-Zeeman Institute in Amsterdam uses a gas-discharge lamp. However, the Bessy laboratory of the Helmholtz-Zentrum near Berlin uses synchrotron radiation. More detail concerning these two systems is given further down in chapter 3.

After the monochromatic light of the wanted wavelength strikes the sample, the photoelectrons are ejected into the vacuum in all directions. By adjusting the angles of the sample holder, one can choose to detect for electrons with the $k$-value one is interested in. These photoelectrons are then collected in the analyzer, which consists of an electrostatic input lens, a hemispherical deflector and an electron detector.

The role of the electrostatic lens is to focus and decelerate the incoming electrons onto the entrance slit.

The heart of the spectrometer is the deflector, which consists of two concentric hemispheres with radii $R_1$ and $R_2$. Between them is a potential difference $\Delta V$, making it a capacitor. By tuning this potential difference to a precise value, one is able to exactly select electrons certain of a given kinetic energy. This energy is calculated through the following equation:

$$E_{\text{pass}} = e \Delta V \left( \frac{1}{R_2} - \frac{1}{R_1} \right)$$  \hspace{1cm} (2.12)

These electrons can then be run through an electron multiplier, followed by some kind of electron counting device. Contemporary setups usually make use of an electron multiplier with a CCD behind it, linked with a computer software package for further evaluation of the collected data.
Chapter 3

Connecting theory with experiment and vice versa

In section 1.1 primarily introduced was the theoretical concept of superconductivity, and after that it dealt briefly with a framework in which HTSC tends to be described nowadays. Secondly, the jump in chapter 2 was made to the background of the tools, that are being used within this research, aimed at improving our understandings of high \( T_c \) superconductivity.

Now that some understanding of most of the theoretical aspects that are involved in this research has been provided, and of the tools that connect one with them, this is going to be linked with the actual experimental environment, and the experimental setup and methods of measuring used.

What first will be done, is connect the relevant physical quantity one is able to measure with ARPES, with the so called superconducting order parameter, which possess a symmetry in \( k \)-space, one can experimentally verify. This is done in section 3.1. Hopefully it provides the reader with some understanding and basis, for the research that has been carried out. After the reader was given some insight in the connection between how a theoretical approximation of nature can be put to the test and thus verified in nature through experiment, continued is with describing the samples used, and the machinery used to perform LEED and ARPES. This is done in section 3.2. After that, an elaboration follows on how was measured, and how the experimental data achieved was processed.
3.1 Linking the superconducting gap with the order parameter

What is learned in chapter 1.1.1, is that there exists a superconducting gap, which shows up as a shift in the leading edge of the Fermi surface. Furthermore, it was seen in section 1.1.3, that the macroscopic phenomena encountered in superconductivity, are described by a so called order parameter, which tells one a lot about the collective behavior of the electron system in a material.

Now by using contemporary ARPES measurements, the superconducting gap may be experimentally verified. By doing measurements at the right kinetic energy, one can measure the \( E(k) \) relations close to the Fermi level. So doing, one can actually "see" the electron bands within the material, terminating at a certain energy, called the Fermi energy, or \( E_F \). The electron occupancy near the Fermi energy (or Fermi surface if one considers the boundary between occupation and non occupation over the three \( k \)-dimensions of a real solid), is the well known Fermi-Dirac distribution, due to the Pauli exclusion principle. By slicing through the band-structure of the material near the Fermi-surface with multiple ARPES measurements, one has a very strong tool in determining the superconducting gap as a function of position in \( k \)-space. Just determine the shift of the leading edge of the spectrum, away from the Fermi energy, see Fig.3.1. More on this further down in section 3.3.

![Figure 3.1: Two plots showing pictorial the electron occupancy near the Fermi energy. Left: "Normal" occupation in a material not in a superconducting state. Right: Material is in superconducting state, and the Fermi-Dirac distribution is symmetrized around the Fermi energy, showing a gap of magnitude \( 2\Delta \).](image)

What would be interesting is to understand what mechanism causes this shift in the leading edge. As was learned in section 1.1, it is possible for two electrons with equal but opposite \( k \)-vector, to bound in pairs and thereby lowering their energies. Because electrons are two \( s = \frac{1}{2} \) fermions, they need to obey the Pauli exclusion principle, which placed them at the Fermi surface in the first place. However, by pairing into a combined state, their mutual spin is now the singlet \( S = 0 \), so by forming a composite boson, the two electrons are no longer required to be at the Fermi level, dropping out of the fermionic problem and pair into the delta function representing the bosonic condensate. In other words, the fact that electrons as fermions "disappear" from the Fermi surface, manifests itself in the forming of a gap in the single particle excitation spectrum, shifting the leading edge away from the \( T > T_c \) Fermi surface and towards higher binding energy \( E_B \).

However, the important thing to notice, is that the superconducting gap is directly linked to the geometry in which the superconducting order parameter manifest itself. In other words, the symmetry of the order parameter \( \psi(k) \) throughout reciprocal space, can be determined by quantifying the superconducting gap \( \Delta(k) \). This is not too hard to see, by loosely considering the following
argument.

The absolute square of the order parameter $\psi^*(r)\psi(r)$ - see equation 1.7 - is equal to the pairon density at field point $r$. For conventional superconductors, which possess an $s$-wave reciprocal order parameter symmetry (meaning total rotational symmetry), the pairon density described by this order parameter is constant throughout the field. However, as stated earlier, HTSCs do not in general need to have $l = 0$ symmetry for their order parameter. This means, that when looking at the absolute square of $\psi(r)$, the pairon concentration can be more dense at certain points in this field, according to the symmetry of $\psi(k)$. At these points, more electrons have left the Fermi surface to form the pairons, observed as the higher local pair density, thus we observe a bigger gap in the single particle excitation spectrum.

Getting back to the experimental environment, by recording how the gap changes while navigating throughout $k$-space, one knows the superconducting gap $\Delta(k)$, which possess a certain symmetry in $k$, from which again one knows the $\psi(k)$ which shares the same symmetry. Thus, simply by looking with ARPES throughout $k$-space, recording the gaps at the angles one measures at with the analyzer (see equation 2.10), thereby determining $\Delta(k)$, one has a very strong tool in qualifying the symmetry of the superconducting order parameter, which is a physical quantity of much importance in quantum electron matter research. However, the reader must be warned that by utilizing ARPES, one looks at the absolute square of the superconducting order parameter, $|\psi(r)|^2$, which is the local pairon density. This makes ARPES not phase sensitive, and the sign of the, or any shifts in phase stays undetermined.

This last section is quite crucial in understanding what one is actually measuring, and to understand and interpret the results that will be presented in chapter 4. Hopefully the reader now understands, that the measurements carried out have no real footing in the familiar three dimensional space, one experiences all around. On the contrary, measurements are carried out in $k$-space, which tells a lot more about the characteristics of the superconducting samples. More on this in section 3.3. The fact that the geometry of the order parameter can be verified, by looking at the band structure of a material, makes it one of the corner stones in the research into contemporary high temperature superconductivity. Every theory trying to explain the electron correlation within high temperature superconductivity, is able to produce a symmetry in which the order parameter should present itself to us. This makes probing the symmetry of the order parameter one of the litmus tests for every theory in the field of correlated electron superconductors.

3.1.1 The prediction of further breaking of $d$-wave symmetry into $d+s$.

As will be looked further into in section 3.1, a theory of superconductivity can be put to the test by looking at the symmetry of the order parameter, through experimental determination of the gap function. For the cuprates, it is found to be $d$-wave, and the number of experimental verifications of this symmetry over the years is quite large. When considering the $SU(2)$ slave boson theory by Wen and Lee [11], which rests on the twin pillars of the $t - J$ hamiltonian and the RVB state, this symmetry is either $s$-wave or $d$-wave as discussed earlier.

However, when taking the viewpoint of Zaanen et al., they predict that the symmetry should present itself as $d + s$, were the $s$ component is induced by doping charge carriers in the material.
induced s component thus further breaks the symmetry of the conventional superconductors, giving a situation in which the nodes in the superconducting wave function are not located at the diagonal of the 2D Brillouin zone resulting from the crystal symmetry of the CuO$_2$ plane. The absolute square of the superconducting order parameter becomes single axially broken due to the sign of the d-wave, as can be seen in Fig.1.8. This would result in a shift of the point of zero gap out of the nodal (which is the point found by extending a line from the gamma point in Fig.3.2 to the ($\pi$, $\pi$) point through the band) direction in Fig.3.2 (left). However, it is assumed that within bulk material, an effect will occur called “twinning”, which breaks the symmetry biaxially, resulting in two points around the gamma-($\pi$, $\pi$) point in which a zero gap would be found. Moreover, this would induce a non zero gap at the node, forming a symmetry as in Fig. 3.2 and 1.7.

![Figure 3.2](image)

Figure 3.2: The red line indicates the value of the gap parameter along the electronic dispersion at the Fermi surface of Bi2212. In the left image the way d-wave gap symmetry is measured along the Bi2212 dispersion with a zero gap parameter at the node. The right image depicts how d+s wave symmetry of the gap parameter should represent itself through measurements.

### 3.2 Elaboration on our samples and used facilities

In the section at hand an overview will be given on the experimental parameters, setups and methods used for producing the analysis and results in chapter 4. The following section is largely based on data derived from the masters thesis by S. de Jong [15].

#### 3.2.1 The HTSC Bi2212 samples

In the experimental verification of the prediction by Zaanen et al., slightly lead doped Pb$_x$Bi$_{2-x}$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Pb-Bi2212) samples were used, more often just referred to as Bi2212. The lead doping is important for making the experimental analysis less difficult, because it suppresses a modulation, present in pristine Bi2212, which has a periodicity of around five unit cells, and is due to a slight mismatch in in-plane dimension of the BiO layers compared to the other layers in the compound (SrO, CuO$_2$, Ca). The use of Pb-doped crystals translates into experimental data which show less distortion of the bands with superstructure, and overall makes sure that the data is more...
well defined. The crystals we used for our research had a superconducting transition temperature of around 68K, compared to a maximum critical temperature at optimal doping of around 95K.

The electronic structure and properties of Bi2212, are largely determined due to the fact that it is a p-type superconductor. This means that its superconducting properties are believed to be explained through the amount of oxygen that is doped within the crystal structure. The oxygen resides in the insulating BiO planes, acting effectively as a charge reservoir. In this manner one is able to dope holes into the CuO planes, and the amount of oxygen that is doped within the structure, is given by $\delta$ in the structure formula of Bi2212: $Bi_2Sr_2CaCu_2O_{8+\delta}$. These hole reservoirs are the providers of the charge carriers we stumbled upon earlier in section 1.3, which are mobile within the AF background.

![Figure 3.3: Schematic plot of the Fermi surface of Bi2212, indicated with the $\gamma$ point, and the M points at (0, $\pi$) and ($\pi$, 0) and the Y point at ($\pi$, $\pi$). For simplicity the c-axis bilayer splitting is disregarded.](image)

Also, between the BiO planes of subsequent unit cells, there are only weak van der Waals bonds, making the resistivity in the $c$ direction within the crystal much higher than in the $a$, $b$ plane. This also makes cleaving of Bi2212 quite easy, because a strip of one or several unit cells thick is easily peeled off the crystal, leaving a clean and flat surface behind most of the times.

Let’s now make the leap into reciprocal space. The Brillouin zone of Bi2212 can be approximated by a two dimensional reciprocal unit cell, spanned by $a^*$ and $b^*$. This is because the Fermi surface of Bi2212 is almost a cylinder, extending in the $k_z$ direction, making the dispersion in the $k_z$ direction almost constant and thus of negligible effect on the measurements. Because we have two CuO$_2$ layers, with in between a calcium atom, the electronic dispersion of the electron residing in the CuO$_2$ planes, splits in a bonding and anti bonding band, both crossing the Fermi surface of the compound. This is due to the fact that wavefunction of the electron can be in phase with the two CuO$_2$ planes, resulting in a higher probability to reside on one of the two planes, or in anti-phase, which places the electrons probability at the Ca atom.
3.2.2 The FOM Amsterdam Momentum Space microscope

The FOM Amsterdam Momentum Space microscope (FAMoS) is the facility for angle resolved photoemission measurements, situated at the van der Waals-Zeeman institute in Amsterdam. It consists of two chambers: a main chamber and a preparation chamber, both under ultra high vacuum (UHV). The preparation chamber is, besides being used for cleaving the samples, also used for doing LEED on the samples. Next to the main and preparation chamber, there resides also a load lock, to insert fresh samples ready to be cleaved. The volume of this load lock is quite small compared to the other two chambers, so it is not necessary to do a bake out after every new batch of samples is placed in the load lock. The main chamber is also shielded against induced magnetic field from external sources. In this chamber one finds the entrance to the electron analyzer of a Scienta type, and a Gammadata VUV high intensity photon source.

The electron analyzer consists largely of two important parts. The first part the emitted photoelectrons encounter, is a system of subsequent electrostatic lenses, which enables to select for certain ranges of angle, which can be translated into crystal momentum $k_{||}$. By changing the potential within these electrostatic lenses, the Scienta can discriminate between different emission angles, and thus for different values of $k$ - see equation 2.10 - and collect these electrons separately yet at the same time. The second part of the Scienta is the hemispherical analyzer, which consists of hemispherical metal plates, between which the photoelectrons travel. These work as a capacitor by applying a voltage difference over them, and thus discriminate for the energy of the emitted photoelectrons. This enables the user to plot graphs, both in the $k$ range and in the energy range, giving thus useful information about the electronic dispersion relations within the analyzed sample. The electrons are then run through an electron multiplier and detected with a CCD and a phosphor screen. There is also a so called Scienta slit, which is a slit that can be opened or closed, which has its impact on the counts of course, but also on the resolution one measures with.

The light source is of the Gammadata VUV high intensity photon source model, as mentioned earlier, and works by igniting highly purified helium gas, creating a plasma that rotates inside an applied magnetic field. By exciting this plasma with an external electromagnetic field (microwaves), electrons within the plasma will photons with an energy equal to the HeI $\alpha$ (21.2eV) transition or the much weaker HeII $\alpha$ (40.8eV). This light passes through a monochromator, to make sure that only light of the right wavelength enters the main chamber. This reduces the background in the measurements.

The manipulator that holds the sample has six degrees of freedom. Three translational ($x, y, z$) and three rotational (polar, azimuth and tilt). Its function is also to cool the sample, down to a minimum temperature of around 14K. This is done by connecting it to a liquid helium bath at 4.2K. Around the sample one finds a thermal shield, to protect the sample from black body radiation, and a heating element, which can heat the sample to a temperature of choice, above 14K.

3.2.3 BESSY at the Helmholtz-Zentrum, Berlin

For the research carried out in this project also the synchrotron BESSY near Berlin was used for measurements, courtesy of the Helmholtz-Zentrum Berlin. The advantage of measuring with a synchrotron is the flexibility in photon energy one can measure with. The light intensity is high,
the user is able to measure at photon energies for which, for instance, the anti-bonding bands are better visualized. In short, the light is obtained by putting packets of electrons at relativistic energies within a storage ring. By letting these electrons pass through an undulator, with subsequent reversed magnetic field, the electron bundles are deflected, and start to emit light. This synchrotron radiation passes through a monochromator, and then reaches the experimental setup.

The measurements presented in section 4.2 were obtained at the UE112-PGM2 end station 13, "one-cubed", at BESSYII. The sample can be moved over four axes, three translational and one polar angle. It is in theory possible to also move the sample over its azimuthal axis, by lowering it down again into the transfer position. However, in practise this was not advisable, due to the fact that securing the sample again for measuring would alter the azimuthal orientation again in a non anticipative way.

The 13 system, in theory, is capable of delivering three interesting experimental parameters, namely: a light source resolution of 1meV, an electron analysis resolution of 1meV and a sample temperature of 1K. However, in practice one was able to achieve a resolution of around 10meV. The factor ten lower resolution was because of misalignment of the light source with the focal point of the Scienta and sample. It should be noted that doing ARPES at a temperature of 1K is a unique experimental parameter, world-wide. This places the 13 system at this moment right at the top of ARPES capable facilities.

Normally, one would first try to get the highest photoemission counts by optimizing for Keithley current (a measure for the light intensity reaching the sample), and then optimize the counts by moving the whole main chamber, together with Scienta to get coincidence of the light spot, the Scienta focus and the center of the sample. Though this was impossible due to the heavy load of the 1K cryostat on top of the main chamber, and the fact that the light beam had to pass through small holes in the thermal shielding of the sample. This misalignment sometimes made the manipulator touch - probably - the thermal shielding while translating on the y-axis looking for the sample and keeping it in focus while measuring. It is suspected that this also altered the orientation of the sample along other axes. When looking at the blueprint of the manipulator and the way it was connected with the cryostat on top, it rises suspicion that the sample makes a pendulum like motion through the thermal shield, because it had to be refocussed after every movement over the polar axis.

3.3 Measuring on Bi2212: Methods and procedures

The main concern in this project, was measuring the k||-dependence of the superconducting gaps in our samples in a secure way. This was done through the method of minimum gap locus. Let’s first introduce some terms, associated with ARPES measurements, see also Fig.3.4 for clarification. The output of the Scienta is a momentum distribution map (MDM). It is a three dimensional plot of the number of photoelectrons that reached the CCD as a function of energy and momentum. This MDMs consist of slices stacked horizontally and vertically, both giving different information of the electron occupancy at the angles we measured at. Stacked vertically, we have plots called electron distribution curves (EDCs), which plot the electron occupancy (the intensity of emitted photoelectrons) as a function of energy for a particular value of k||. The other information is contained in momentum distribution curves (MDCs), stacked horizontally, which plot the electron occupancy
against the angle along the Scienta slit, which can be converted into values for lattice impulse. The MDC is a constant energy quantity.

![Figure 3.4: Figure depicting how the EDCs and MDCs are extracted from the MDM (a) which is the output of an ARPES measurement. (b) shows an MDM, taken along the purple line in (a), (c) shows the EDC, taken along the green line in (a).](image)

Now for the determination of the gap, one is mostly interested in the EDCs, because they show directly electronic distribution in $E$ around $E_F$ - i.e. at the Fermi surface. The method consisted of first determining the minimum gap, hence the name of the method. This was done by symmetrizing the MDM around the Fermi energy, and look for the also symmetrized EDCs containing the electron band information. By going through the subsequent slices, it can be determined which EDC gives the minimum gap, which is the gap showing the least deviation on both sides from the Fermi energy. This EDC, the unsymmetrised, original version was then plotted against a gold reference. Finally the deviation of the leading edge of the Bi2212 EDC leading edge away from the leading edge of the gold reference, was taken as the superconducting gap in units of eV.

The gold reference was taken on a gold film, that had been evaporated onto the clamp keeping the sample attached to the manipulator (FAMoS), or onto the sample holder ($1^3$). Both the clamp and the sample holder of the two different setups, where at the same temperature as the sample itself and were at good electrical connection with the sample, thus making sure that we were not normalizing with a faulty reference. Besides delivering the reference leading edge for determining the value of the measured gaps, the gold reference was also used for normalizing the MDM for any detector spots and/or misalignment.
The position at which the gap was taken, can be plotted in different ways, namely through the use of a Fermi surface angle, or through the use of a Fermi surface map. The Fermi surface angle is a more theoretical construct, and is an insightful way of positioning yourself in $k$-space. In the measurements carried out at the FAMoS, this construction was used because the Fermi surface maps had not enough quality to plot the positions in $k$-space in a convenient way. At FAMoS, measuring was done by aligning the Scienta slit precisely along the nodal region of the dispersion at the Fermi surface, and by altering the tilt, which effectively translates the slit in a direction perpendicular to its opening. For this method it is necessary that the azimuthal orientation along the nodal direction is determined with great precision, so one can use the following equation that can be found after doing some basic goniometry:

$$\theta(t) = \frac{360}{2\pi} \arcsin \left( \sqrt{\frac{1}{13}} \right)$$  \hspace{1cm} (3.1)
with $\theta$ the Fermi surface angle and $\ell$ the tilt in degrees (where the maximum tilt is 13 degrees).

To determine the azimuthal orientation for the slit along the nodal point\footnote{which is the point where a line going though the gamma point and the X point crosses the electron dispersion}, LEED is the best option, because it is a measurement which is uncoupled from any use of ARPES, so it is a fair way of orienting the sample. This was done by doing a LEED measurement in the preparation chamber, before starting any ARPES, by aligning the intensity spots seen on the computer screen by turning the azimuth.

For the orientation in $k$-space of the $1^3$ measurements, use was made of a Fermi surface map, which could be made with great precision due to the high photon energy one can measure with. By using high photon energies, a broad slice of $k$-space is shown along the Scienta slit. Then by moving the polar, one can map the Fermi surface in reciprocal space. In this manner, the nodal direction can be identified from the form of the Fermi surface and the location of the high symmetry points.

Because the axial orientation at $1^3$ is only adjusted by a polar angle, the MDMs were made by adjusting over the polar range. Because of the orientation of the Scienta against the light source, the polar angle at $1^3$ translates into the same tilt measured with at FAMoS; a movement perpendicular to the slit orientation.

The samples were cleaved in situ. This was done for the FAMoS by removing a tesa loop, that was attached to the sample outside the load lock. By removing this tesa loop in the preparation chamber with a special arm, one can peel off a slice of Bi2212, thus making sure the surface left on the sample holder is flat and without any oxidation or contamination. Cleaving at the $1^3$ was done by gluing a so called top post on the sample, which is a more rigorous way of cleaving, actually more suited for cleaving pnictides. However, at the $1^3$ there was no way in which one could peel off any tesa loops, so it was decided to apply the top-post method regardless. The top post was then removed in situ by knocking it off the sample holder it with one the manipulator arms.
Chapter 4

Results of our study on Bi2212 and discussing the obtained data

Finally one has come to the point that one is in a position to examine the gathered data, through hopefully a firm understanding of concepts and tools, so one is able to understand the analysis carried out of the data. The first section 4.1 will treat the results obtained at FAMoS, and the section following it, section 4.2, the results obtained at Bessy.

The weight of the analysis on the gathered data will also be on this last section, because the quality of the data recovered at BESSY, is for the purposes of the research to be carried out far superior to the data obtained at FAMoS. Though, for completeness because the research was initially to be carried out at FAMoS, and also in contrast of what one is capable of by utilizing a synchrotron, it was chosen to include the FAMoS data from the best data set we achieved. However, the FAMoS data set will only be briefly discussed, so as to use the space available to concentrate on the BESSY data.
4.1 Results obtained at FAMoS

In the following section the best data set achieved with the FAMoS will be presented. A profound analysis and discussion on these results will not be carried out as mentioned above.

The following data was obtained at a temperature of $30 \pm 8K$, where the uncertainty in the temperature is this high because of the fact that the liquid helium was depleted at the half of our measurements, and the sample started to warm up.

The quality of the data is quite bad, as can also be seen from Fig. 4.2, this is probably due to a bad sample. However, the quality of the LEED in Fig. 4.1 seems to be quite good, with not too much superstructure.

Figure 4.1: LEED image of the sample used in the ARPES measurements at the FAMoS system, taken with an bundle energy of 110 eV.

Figure 4.2: Waterfall plot of the leading edges on which the plot was based of the gaps, see Fig. 4.4. Going from right to left through the measuring points in that figure corresponds to the EDCs from bottom till top in this figure.
In Fig. 4.3 three different MDMs are presented which belong to the data set from which the gaps in Fig. 4.4 were deduced. On the associated EDCs can be seen, which are plotted underneath the MDMs, that the statistics are not really good, and that one also not observes any superconducting peaks (the called coherence peaks). This despite the fact that the Bi2212 were well within the superconducting phase in terms of the sample temperature.

Figure 4.3: Three MDMs of electron bands we measured with FAMoS. Under each MDM we plotted the EDC which was used for determining the gap against the Fermi level of each band. The left EDC was taken at FSA=0 degrees, the middle one at FSA=-4 degrees and the right MDM at FSA=-26 degrees.
Figure 4.4: Our results of our analysis on the superconducting gap, taken from the EDCs shown in Fig. 4.2.

Concluding on this data set is that one is not able to trust the gaps measured (if any). The procedure followed to include the error bars is explained further down in section 4.2.
4.2 Results obtained at Bessy

Figure 4.5 shows the Fermi surface map of the sample used at the PGM2 end station at Bessy. It was taken at a photon energy of 50eV with a 100µm exit slit, and a rather big Scienta slit of 0.5mm curved, by letting the polar angle of the sample run from −17.5° in steps of 0.75° to 10.25°. Then by interpolating and summing between consecutive slices, the images was smoothened. This enabled to make a quick scan of the Fermi surface, keeping one from not to waste too much time on data that was just collected for orientation, and aging the sample unnecessarily. Also, a gold reference scan was made, which enabled to normalize the data as regards the correct Fermi energy position, detector misalignment and dead spots. The gold was evaporated in situ in the load lock on the sample holder, before cleaving the sample. The temperature of the sample was around 26 ± 0.05K, so already well within the superconducting state.

Figure 4.5: Plot of the Fermi surface of Bi2212, created by moving the polar angle over 27.75° in steps of 0.75°. Compare to Fig. 3.3.

The first thing directly observed, is that around the nodal area - see the arrow in Fig. 4.5 - a sudden shift in the \( k \)-value of the data is seen. This seems to be the case for all the counts along the Scienta slit in that slice, see for instance the shadow bands of the Bi2212 sample, which are the flipped and less intense bands next to the red intense bands. It would be best, to first take a closer look at this anomaly, before to continue presenting data on measuring gaps etc.

Figure 4.6 shows two different plots of momentum distribution curves (MDCs). They were taken from the data to the left, right and at the arrow in Fig. 4.5. A MDC shows us the relative photoelectron intensity along the slit of the Scienta. So a MDC determines the \( k \)-value for the emitted electrons, for a certain energy. In our case we took the MDCs at the Fermi level (see the black lines in Fig. 4.7).
Figure 4.6: Two plots containing Momentum Distribution curves of the collected data, next to the angle at which the angular jump in the data appeared. (a) shows us a stacked plot of five MDCs, with the blue MDC clearly shifted against the MDCs at polar angles above and under it. (b) shows the left part of Fig. (a) in a waterfall plot.

Figure 4.7: Three Momentum Distribution Maps (MDMs), with in the middle the MDM of the shifted data set, with on its side two adjacent polar angles. In the lower part we see the three MDCs belonging to their MDMs above.

When comparing to its neighbors, it can be seen that the shift in angle along the Scienta slit, is in the order of 1 degree. This distortion is assumed to show up because of the construction of the $1^3$. Its alignment was quite out of focus with the Scienta and light source. So sometimes when moving the sample within the space of its thermal shield, it would hit the side of this shield. It is assumed
that by turning the sample over its polar axis, the sample makes some kind of pendulum movement within the thermal shielding tube, and that at the angle where the shift shows up, the sample hits the shielding, thereby altering its angles, what we observe as a sudden shift in apparent $k$ position.

However, when examining Fig. 4.7, one sees that qualitatively the MDM’s share the same quality. Also, it is observed that no alteration of the electron distribution and/or overall bandstructure is visible.

The fact that the data within each cut are of high quality and are only shifted in angle is not an enormous handicap as one is not that much interested in distribution in momentum at first instance, as long as the dispersion in energy $E$ is determined with great precision. When considering the experimental analysis to be carried out, and what data to subtract from the MDMs - namely energy distribution curves (EDCs), which are perpendicular to momentum distribution curves - it is not felt that this overall shift in $k$ will be of great impact on the analysis, because the gaps will be measured by the method of minimal gap, more on this further on in this section. So consistent and trustable results along the energy axis have priority, and the observed shift is not expected to alter the leading edge of the Fermi surface, thereby not altering the measured gap size, and thus the determined order parameter symmetry.

Now that the position in $k$-space is known through the Fermi surface map, a measuring strategy is set up, and the experimental parameters are determined. It was chosen to stay at the photon energy of 50 eV, but took a Scienta slit of 0.2 mm curved, and also a much smaller exit slit on the monochromator of 40 µm, along with an Angular30 mode on the SES. The first two changes improve the energy resolution and the 40 µm exit slit also improves the $k$ resolution perpendicular to the slit. Also was decided to focus the measurements around the nodal region, and to start from $\theta = -15^\circ$, going up in steps of 0.5°, because it is around the nodal region were the breaking of $d$-wave symmetry is supposed to be seen. See Fig. 4.8. The sample was also cooled down even further, to reach a stable temperature of $T = 1.26 \pm 0.07 K$. 
Figure 4.8: Map (still at 26K) of our measuring strategy. The white arrows indicate our initial measurements, the yellow arrows our second run over the region. Our initial measurements were taken between $\theta = -15^\circ$ and $\theta = -6.5^\circ$. Our second set of measurements was in the region $\theta = -11.75^\circ$ and $\theta = -9.25^\circ$.

The Bi2212 sample used, had a $T_c$ of around 68K which is 37 K under optimal doping, so slightly overdoped. The cleave was done still at room temperature. It is more common, to cleave in the main chamber, however, when placing the sample in the main chamber, it immediately starts to cool down because of the design of the 13. Having no real experience in cold cleaving Bi2212 in this system, and because our first cleavage attempt was a "cold" one and dit not result in a "good" cleavage surface, a room temperature cleavage strategy for the data presented here was decided upon.

The measurements were begun by doing a gold reference. To get enough statistics took about twenty minutes. However, while doing measurements on Bi2212, gold references were continued to be made every three measurements. This was done, as it had been suggested by the beam line scientist, that it could be that through the misalignment of the 13, the leading edge of the Fermi level could shift in time. This would of course be disastrous for any measurements on a gap, as it would instantly create gaps, so it was decided to keep track of any possible shift in the leading edge of the gold. Only shifts in the leading edge were of interest, resulting in a need for less statistics and enabled to do the gold references quicker than the first one. Every vertical slice of the MDMs were then summed, and compared to the earlier gold references. The results of these reference measurements can be seen in Fig. 4.9 (a) and (b).
Figure 4.9: (a) Graph of the angular summed EDCs of our gold references, taken at different values for $\theta$. The EDCs were collected by summing all the slices for different $k$, and then taking a cut through the energy regime for constant $k$. (b) is the enlarged plot of the area indicated by dashed lines in (a). From this plot it can be told that the maximum difference in Fermi energy is not more that $0.0005 \pm 0.0003$ eV.

Observed is that there is almost no time dependence in the position of the Fermi level. The measured discrepancy between the two measurements showing maximum difference, number 42 and number 72, is not more than $0.0005 \pm 0.0003$ eV. To compare with this, the width of the leading edge between 0.1 and 0.9 relative intensity is in the order of 0.015, which differ a factor 30.

Next the results of the gap measurements are presented. This was done through the method of minimal gap, see section 3.3 for a more in depth treatment of this method.

Let's first focus on Fig. 4.10(a). It plots the value of the gap in meV, against the polar angle the MDM was taken on. The error bars were achieved in the following way: for the $x$-axis, a constant of $\pm 0.25^\circ$ was taken, because the polar position at which one would slice the nodal area was uncertain in $0.5^\circ$. The $y$-axis error was taken, by looking first for the uncertainty in which it was possible to determine the minimal gap from the symmetrized EDCs. Then the EDC of that slice was taken were the gap was thought to be minimal, and the EDC of the slice of which it was quite certain that the gap was opening up again, thus being no minimum gap. Then these EDCs were plotted in one graph, and the deviation measured of the two leading edges from each other. This method enabled to determine the uncertainty in the gap for every MDM.
Figure 4.10: (a) shows the leading edge superconducting gap as a function of the polar angle. Around a polar angle of -10.5, a clear anomaly is observed. The solid black dots are from the first measurements, the open dots from the second set of measurements. (b) is a plot of the EDC’s, pertaining to the data point in (a). Here also one can see the closing gap at -10.5 degrees.

Figure 4.10(a) is a little bit stretched to the left and right, thus giving a light distortion in the geometry of the $d$-wave, because it was plotted against the polar angle, and not against Fermi surface angle. Fig. 4.10(b) shows the EDCs next to each other from which the gap measurements were taken. Also, plots (a) and (b) consist both out of two different runs of measurements. What is observed is that there seems to be a "positive gap". This however is due to the fact that the higher density of states around the superconducting peak is being cut off by the Fermi-Dirac distribution, which shifts the leading edge resulting in the measurement of positive gaps. The solid dots were the measurements, following from the initial measuring strategy. However, the open dots are measurements from the second run on the same sample, which are shifted by 0.25° in polar angle against the first routine, but the subsequent measurements were kept 0.5° apart.

The first thing noticed, is that the $d$-wave pairing symmetry seems to behave quite as it should around the nodal point, which is located at or around a polar angle of -13 degrees, because that is the position at which the shadow band and "normal" are the most apart. The initial thought on this was that so far the results on $d + s$-wave pairing symmetry would be inconclusive. However, upon continuing the measuring strategy, a point was reached were it was realized the pairing symmetry
was not purely $d$-wave. Through the analysis carried out at the same time of measuring, a peculiar bump showed up around $\theta = -10.5^\circ$, were the gap seems to be closing up again. When noticing the closing gap, it was decided to run a second set of measurements, to gather more data around this point. So we noticed the closing gap further down our first measuring strategy.

As one can see, the closing of the gap was in our first run of measurements only noticeable through the unusual shift of just one point. It was thus of great importance to include the second set of measurements, to know if it was just a misaligned detector, or maybe a faulty measurement with unusually wide error bars. However, upon doing the second polar run, it showed the same tendency towards a partial gap closing at $\theta = -11.75^\circ$ and $\theta = -11.25^\circ$. It is quite reassuring that in both data sets, the gap anomaly shows up around the same Fermi surface location. This gave the observation a bit more quantification, also due to the fact that the other data points seem to line up quite nicely with the first data set.

Figure 4.11 shows a waterfall plot of the same data used to obtain Fig. 4.10(a) and (b). It is shown to compare the different EDCs used to obtain the data points of 4.10(a). One can see that the EDCs all share the same quality, with enough statistics on the leading edge, to make a good measurement of the leading edge.

The following Fig. 4.12 was created upon further investigation of the MDM around the area in which the gap anomaly was observed. Figures 4.12(a), (b) and (c) show a portion of the MDM around the band, for three polar coordinates: $\theta = -12.0^\circ$, $\theta = -11.5^\circ$ and $\theta = -11.0^\circ$. Figure 4.12(d) was then created by taking the MDCs of these three MDMs for a constant energy of $-0.015eV$, and plotting them in the same graph. What is observed is a certain shift in weight of the electron bands. The red curve in (d) seems to have a Lorentzian form, an electron distribution expected in $k$. However, when moving up to polar angles $\theta = -11.5^\circ$ and $\theta = -11.0^\circ$, it is of course noticed that this shape shifts to the left, which is in accordance with the $E(k)$ dispersion relation of Bi2212, but also a distortion of the MDC shape where the peak of the Lorentzian form shifts to the left with
Figure 4.12: (a), (b) and (c) showing MDMs of the electronic structure in $k$ space around the angles for which the anomaly in the gap versus $k_\parallel$ was found. (d) is a composed graph of the MDCs, taken from the three MDMs in (a), (b) and (c), at an energy of $-0.015\text{eV}$.

A first thought on this observation is that the anti-bonding band, which runs at this location in $k$-space quite parallel to the bonding band which we observe strongest at this photon energy, is undergoing some kind of transition through the bonding band to the other side of it.

Next in Fig. 4.13 the results on a reference measurement that was done on our Bi2212 sample is shown, to have some quantification on the aging of the sample. The vacuum inside the $1^3$ was not really what it was liked to be, namely in the order of $\sim 10^{-10}$, which is a factor 10 higher than UHV. In addition to that, the temperature of the sample - around 1.25K - was well below the condensation temperature of hydrogen, which is around 20.28K. So it was suspected that the sample could have deteriorated, and thus making the results especially of the second run of measurements less reliable.

The first high resolution measurement was at a polar angle of $\theta = -13^\circ$, so to this angle was returned 4:15 hours later, after the last measurement, to have a reference on the quality of our sample.
Figure 4.13: Figure (a) is the MDM of the freshly cleaved sample and (b) the same place over 4 hours later. Both MDMs were taken at $\theta = -13^\circ$. Figure (c) shows the EDCs of both MDMs (a) and (b), taken at the position along the Scienta slit also used at this polar position for measuring the gap.

Upon inspecting Fig. 4.13(a) and (b) in a more qualitative fashion, it can be seen that the sample stayed quite at the same quality, with still good statistics and low background. Also, when looking at the signal to noise ratio at the leading edge of the two measurements, we see that this is still of rather high quality, and that the deviation between the leading edges in (c) is not more than $0.1meV$, which is still well within range of our error bars in Fig. 4.10(a).
4.3 Conclusion

To conclude this bachelor thesis, the facts obtained in primarily section 4.2 are reviewed, and conclusion are drawn from them, and the discussion held on the analysis.

In first instance, looked was for possible evidence for or against the $d + s$ wave pairing symmetry in overdoped Bi2212 samples. When considering the data above, and especially the plot of the size of the leading edge gap against position in reciprocal space in Fig. 4.10, there are clear signs in the data themselves for an anomalous $\Delta(k)$ behaviour. The fact that the $d$-wave symmetry of the superconducting order parameter in overdoped Bi2212 seems to be broken, is a strong indication of physics yet to be understood. However, the pattern $\Delta k$ follows in Fig. 4.10 is not in complete accordance with the prediction by Zaanen et al.

To be more conclusive, room is seen for a second run of measurements, concentrating strictly for instance in the area around a FSA between -5 degrees and 5 degrees. If this part would be sliced up in a lot of data points, one really is able to focus around the point in reciprocal space the $s$-wave admixture is supposed to show up. Finding a non zero gap in this region would put the prediction by Zaanen et al. on a more stable experimental basis, and would give reason to extend this region step by step to the left and to the right of the node, to map the tendency in which the order parameter evolves around the band structure in this region.

However, during the set of measurements at the $1^3$, the closing of the gap around a polar angle of -10.5 degrees was totally unexpected and deserves more research. It is quite an interesting observation, that the generally accepted $d$-wave symmetry, seems to be broken further. If this of course is confirmed to be true, it would be quite a discovery, and could maybe be a clue lending to a better understanding of the machinery behind high temperature superconductivity.

It was tried to create a bit more understanding of what actually happened at that point, by focussing on the three MDMs right at, to the left and to the right of the point were the gap seems to be closing again, see Fig. 4.12. A first assumption is that there is some kind of shift in weight of the electron occupancy in the bonding and anti bonding electron bands. What causes this transition is not totally clear at this moment. However, a little thought on the closing of the gap, together with the transition of anti bonding and bonding bands, can maybe shed a little bit of light on this matter. If there is some kind of transition of the anti bonding band through the bonding band, the electron occupancy per value of $k$ would increase. However, due to the Pauli principle, this higher local density of electrons places the electrons now sharing the same $k$ value right at the Fermi edge of the band, filling it up at higher energies, which could maybe be observed as a gap that seems to be closing again.

It seems after observing this unexpected breaking of symmetry, that it could be fruitful to further investigate this phenomenon, if it would show up again of course, and is not just an irregularity in our used Bi2212 sample. An idea is to move to another photon energy, other than 50eV, in which the anti-bonding band is better resolved. Then by focussing around this point, one could further map the behavior of the anti bonding band. Also, it could be an idea to move to the opposite side of the node, to see if the same tendency shows up there. If this would be happening, then it would place the assumption of a further breaking of the $d$-wave symmetry, not necessarily in $d + s$, on a more solid basis. We tried to do the same analysis we carried out on the bonding band, on the shadow bands to see if they would show the same tendency. However, this was of no use because there was
not enough statistics to determine the gap with a precision that would resolve any bump showing up in the $d$-wave gap along $k$-space.

To conclude this Bachelor thesis with: the experimental verification of a further braking of $d$-wave pairing symmetry into $d + s$-wave symmetry is quite a difficult task, because it is our understanding that there is no prediction whatsoever on the size of the $s$-wave component of the gap or with regards to how smeared out it should be along the nodal region. Maybe this is a good thing, so the experimental physicist is not biased by expectations from the theoretical side of things. However, it makes looking for it like looking for a needle in a haystack. Nevertheless, we would like though to emphasize that, when looking at the results obtained at the 13 end station where the first Bi2212 ARPES data world wide was measured at temperatures as low as 1.2K, the book is not yet closed on the symmetry of the superconducting order parameter in overdoped Bi2212. That maybe $d$-wave symmetry will eventually be a limiting case of a vast amount of theory and concepts, not yet fully understood, and is awaiting even more sensitive and sophisticated experimental exploration.
Chapter 5

Supplementary

5.1 Acknowledgements

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5.2 Dutch abstract

Het onderzoeksveld in hoge kritische temperatuur supergeleiders heeft, naast een duidelijke industriële toepassing - in het vervoer van electriciteit bijvoorbeeld - het potentieel om grote theoretische gevolgstrekkingen te hebben. De controverse die zij meebrengt, binnen ons inzicht in hoe gecorreleerde elektron systemen zich gedragen, zowel op macroscopische als op microscopische schaal, is groot genoeg om een enorme hoeveelheid theoretische output te genereren.

De focus van dit bachelorproject zal zich richten op het testen van een van de meer gewaagde theorieën, voorgesteld door Zaanen et al. [1]. Sinds de ontdekking van hoge-temperatuur supergeleiders, is er een uitgebreide discussie gaande over de symmetrie van de supergeleidende order parameter. Dit is de complexwaardige golffunctie die het gezamenlijke gedrag van de supergeleidende ladingsdragers voorstelt.

Voor een bepaalde klasse van materialen genoemd cuprates, werd een algemene consensus bereikt, zowel experimenteel als theoretisch, dat deze symmetrie d-wave moet zijn. Echter, Zaanen en zijn groep uit Leiden zijn van mening dat door verdere doping van vrije ladingsdragers in deze cuprates,
de $d$-wave symmetrie verder gebroken zal worden in $d + s$ symmetrie. Dit is experimenteel verifieerbaar door the kijken naar supergeleidende gap, die is te meten als een verschuiving van de electronen band, weg van nul bindingsenergie.

Dat deze symmetriebreking nooit eerder is waargenomen komt grotendeels door twee redenen: De theoretische berekeningen zijn simpeler in het het geval van een lagere dichtheid in van vrije ladingsdragers, waardoor deze beschreven kunnen worden als een verdund Bose gas. Ten tweede, uit een experimenteel standpunt, moet het oplossend vermogen van de meetopstelling uitstekend zijn. Het doel van dit bachelorproject is om ondersteuning voor, of argumenten tegen het voorstel van Zaanen et al. te geven.

Voor dit bachelorproject is gebruik gemaakt van $Pb_{x}Bi_{2−x}Sr_{2}CaCu_{2}O_{8+δ}$ kristallen waaraan door middel van angle-resolved photoemission spectroscopy (ARPES) gemeten werd. Voorts zal er ook een overzicht gegeven van de theoretische constructie achter het beschrijven de cuprate supergeleiders. Daarnaast is er ook een hoofdstuk bijgevoegd met theorie en experimentele opstelling van LEED en ARPES. Na het verbinden van theorie met de experimentele omstandigheden, zal geconcludeerd worden met de verkregen data, resultaten bediscussieerd en conclusies getrokken.

5.3 Popular Dutch abstract

Hoge temperatuur supergeleiding en de zoektocht naar symmetrieën in het gedrag van electronen.

Supergeleiding is een interessante fase der materie die binnen bepaalde (niet persege geleidende) materialen voorkomt zodra deze worden afgekoeld onder een bepaalde kritische temperatuur. Geleiding kennen we uit het dagelijks leven van bijvoorbeeld electriciteit snoeren die in ons huis apparatuur met het stopcontact verbinden. De weerstand en stroom in deze snoeren veroorzaken een potentiaalverschil volgens de wet van Ohm. Voor supergeleiders geldt echter dat zodra de kritische temperatuur is bereikt, deze weerstand volledig wegvalt waardoor er dus geen energie meer verloren gaat in het opwarmen van de geleider door weerstand.

Hedendaagse supergeleiders kunnen grofweg onderverdeeld worden in de zogenaamde "conventionele supergeleiders" (temperatuur niet hoger dan ongeveer 23K) en de "hoge temperatuur supergeleiders" (denk aan waarden van wel 150K). Deze laatste zijn zowel fysisch als praktisch gezien zeer interessant. Dit komt omdat de theorie die conventionele supergeleiders beschrijft, de hoge temperatuur supergeleiders eigenlijk uitsluit, en deze door natuurkundigen op dit moment nog zeer slecht begrepen worden. Het hebben van een goed begrip over deze materialen zou uiteindelijke misschien wel kunnen zorgen voor supergeleiding bij temperaturen die nog veel hoger liggen, wat bijvoorbeeld positief uit zou kunnen pakken voor de energieverliezen in een hoogspanningsnetwerk. Dit is natuurlijk op dit moment nog verre toekomstmuziek.

De natuur toont zich aan ons in een verscheidenheid aan symmetrieën, zoals de zeshoeken in een honingraat, of de grotere hemellichamen, zoals de aarde, die bolsymmetrisch zijn. Dit alles bij benadering natuurlijk. Ook binnen het onderzoek naar hoge temperatuur supergeleiders komen symmetrieën voor, die verborgen liggen in de relaties die de energie van de electronen beschrijven als functie van hun impuls, wat dispersierelaties worden genoemd. Door zeer nauwkeurig te meten, kunnen deze symmetrieën aan zogenaamde "hoek-oppeloste spectroscopie" ontkraken worden, wat
een zeer belangrijke rol speelt in het hedendaagse onderzoek. Over deze meting verderop meer. Het visitekaartje van een bepaalde theorie die hoge temperatuur supergeleiding hoopt te beschrijven, is namelijk de symmetrie die het voorspelt die verborgen ligt in de electron dispersierelaties van de supergeleider, en deze kan door middel van hoek-opgeloste spectroscopie getoetst worden, wat theoretische voorspellingen verbindt met de fysische realiteit, zie figuur 5.1.

In dit bachelorproject is onderzoek gedaan naar een bepaalde klasse binnen deze supergeleiders, die de naam "cupraten" dragen. Deze naam danken ze aan de één of meerdere koper-oxide vlakken die ze hebben in hun molecuulstructuur. Binnen het onderzoek naar hoge temperatuur supergeleiders gaat men er van uit dat de geleiding van het materiaal voornamelijk in deze vlakken plaatsvindt. Aangezien geleiding wordt veroorzaakt door de beweging van electronen in een materiaal, en weerstand door het botsen van electronen met de kristalstructuur, is het bestuderen van de gedragingen van electronen binnen zo een cupraat van groot belang om meer inzicht te krijgen in supergeleiding bij hoge temperatuur.

Figure 5.1: (a) Een electron dispersie relatie zoals die wordt gemeten in een typisch ARPES experiment. Als je (a) doorsnijdt de diepte in op de paarse lijn krijg je een momentum distribution curve (MDC), figuur (b). Als je (a) doorsnijdt langs de groene lijn, een energy distribution curve (EDC). Deze laatste waren van belang voor dit bacheloronderzoek, aangezien we geïnteresseerd waren naar de verschuiving van de helling in (c) ten opzichte van de 0eV (het Fermi niveau). Dat was waar uiteindelijk de symmetrie in verstoopt zat.

Onderzoek naar de supergeleidende eigenschappen van de cupraten kan onder meer door de eerder genoemde hoek-opgeloste spectroscopie te doen aan deze materialen. Bij deze methode wordt er licht van een bepaalde golflengte (dit hoeft niet persee in het visuele deel van het spectrum te zijn dat wij als mens waarnemen) op het materiaal geschenen. Het fotoelektrisch effect dat hierdoor optreedt maakt dat electronen zich vrij maken uit het materiaal, met een bepaalde impuls en energie. Door deze electronen op te vangen met een detector, en hun energie te meten als functie van de hoek die ze maken ten opzichte van het materiaaloppervlak, kunnen de electron dispersierelaties afgeleid worden, die ons de relatie vertellen tussen impuls en energie van de electronen in het materiaal, zie figuur 5.2.
Voor het onderzoek dat is uitgevoerd binnen dit bachelorproject is van faciliteiten gebruik gemaakt hier in Amsterdam op het van der Waals-Zeeman Instituut, als in Berlijn op het Instituut BESSY II. In Berlijn is zelfs gemeten bij een temperatuur van 1K, wat een wereldwijd unicum is voor de cupraten. Waar op deze beide instituten naar is gezocht in mijn bachelorproject, is experimenteel uitsluitend voor een voorspelling van een theoretisch fysicus uit Leiden. Deze theoretisch fysicus, Jan Zaanen, voorspelt dat onder bepaalde omstandigheden in het materiaal, een breking van de symmetrie optreedt. Wat uiteindelijk is gevonden is daadwerkelijk een breking van de symmetrie, alleen niet geheel, of slechts gedeeltelijk, zoals voorspeld door Jan Zaanen, wat ruimte openlaat voor discussie en interpretatie.

Het één keer waarnemen van een bepaald patroon is namelijk nog niet direct aanleiding dat de theorie waarvan je aan de hand je meting deed, waar is. Zodra het erop lijkt dat je iets ziet dat verband lijkt te houden met de te toetsen theorie, is het zaak om zorgvuldig alle experimentele parameters af te gaan, en te kijken hoe de observatie zich gedraagt als functie hier van. Verder moet een meting natuurlijk ook reproduceerbaar zijn. Jammer genoeg was er binnen dit bachelor project niet genoeg tijd om zorgvuldig de meting te verfijnen, tot op het punt dat je uiteindelijk een goed fundament hebt om bepaalde uitspraken te kunnen doen over het kloppen, dan wel onjuist zijn van de voorgestelde theorie.

Toch is het interessant dat er een breking is waargenomen, aangezien de breking van een symmetrie altijd verband houdt met de overgang van een systeem in een fundamenteel andere toestand. Bijvoorbeeld bij het breken van de symmetrie van ijskristallen naar die van water. Echte maatschappelijke consequenties zullen deze metingen niet direct hebben, aangezien hoge temperatuur supergeleiders daarvoor op dit moment nog te weinig worden begrepen. Toch voegt elke meting weer informatie toe aan de puzzel, wat waarschijnlijk uiteindelijk voor een doorbraak zal zorgen binnen een tak van de natuurkunde waar op dit moment erg veel bedrijvigheid in plaats vindt.

Figure 5.2: Schematische weergave van hoek-opgeloste spectroscopie aan een materiaaloppervlak. Het electron komt uit het sample met een bepaalde energie, en de impuls van het electron kan gerelateerd worden aan uitgaande hoeken phi en theta.
Bibliography


